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COMPLETE SPECIFICATION

Method of Manufacturing Low-Molecular Weight Cellulose Derivatives

We, SHIN-ETSU CHEMICAL INDUSTRY COMPANY LIMITED, a body corporate organised and existing under the laws of Japan, of No. 2, 1-chome Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention concerns a method of manufacturing cellulose derivatives of very low molecular weight, for example, water-soluble cellulose derivatives which, in a 2% aqueous solution, have a viscosity lower than 10 cps at 20° C.

Known methods of reducing the degree of polymerisation of cellulose or its derivatives include cleaving ether bonds between the glucose rings in the cellulose molecule by acid hydrolysis, or cleaving the main chain of the cellulose molecule by oxidation with air or a peroxide or even by mechanical bond cleavage.

However, the above methods are not always performed easily on a commercial scale or suffer from other defects so that at the present time there is not a satisfactory method of manufacturing cellulose derivatives of very low molecular weight on a commercial scale. More precisely, the mechanical process of bond cleavage is so inefficient that it cannot be employed on an economical basis and oxidation by air is too slow. Oxidation by peroxide is quicker but in this method, the removal of the undecomposed peroxide remaining in the product is difficult. Also it is difficult to remove the decomposed material of such peroxides. Other oxidising agents have similar disadvantages.

When cleaving the main chain by peroxides or oxidising agents side reactions also occur, which are also disadvantageous. For example the glucose rings may be oxidised to form aldehyde groups. Also carbonyl groups may be formed in the product by other reactions. The net result is that the product is discoloured and its other physical properties deteriorate thus decreasing its commercial value. In such solution reactions, there is another problem that, as the viscosity of a solution is very high at the beginning, the reaction must be carried out at an inefficient low concentration.

The present invention provides a method of making low-molecular weight cellulose derivatives by partial depolymerisation, which comprises treating, at a temperature lower than 80° C, a cellulose derivative in powder form, with a solution of a hydrogen halide in an anhydrous C_1 to C_6 aliphatic monohydric alcohol, the proportion of hydrogen halide being less than 5% by weight of the cellulose derivative being treated, and subsequently removing the hydrogen halide at least partly in vapour form. If necessary, the product can be neutralised with a weak base after the treatment and the removal of the hydrogen halide. By such a method there can be produced cellulose derivatives of very low molecular weight, without the formation of carbonyl groups, the method being carried out easily and with a good yield of colourless product.

The starting material used in the present invention is preferably an alkyl cellulose, such as methyl cellulose or ethyl cellulose, a hydroxylalkyl cellulose, such as hydroxyethyl cellulose or hydroxypropyl cellulose, a cellulose ester such as cellulose acetate, cellulose butyrate or cellulose phthalate, a carboxyalkyl cellulose, such as carboxymethyl cellulose or a mixed substituted cellulose, for example, methylhydroxyethyl cellulose, methylethyl cellulose, methylhydroxypropyl cellulose, and acetylpropyl cellulose. Mixtures of such cellulose derivatives may also be used.

The hydrogen halide used in the present

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invention is hydrogen fluoride, hydrogen chloride, hydrogen bromide or hydrogen iodide, with hydrogen chloride preferred for reasons of handling, volatility stability, and the cost. When the hydrogen halide is used in excess it is difficult to remove it after the treatment and the product is coloured. Therefore it should be used in a proportion less than 5%, preferably 2%, of the starting material. The hydrogen halide is introduced into the vessel as a solution dissolved in a small amount of C_1—C_6 alcohol such as methyl alcohol or ethyl alcohol in which the cellulose derivative remains as a powder. The treatment should be performed at a temperature lower than 80° C and preferably at 30—60° C. At temperatures higher than 80° C, the treated product is considerably coloured in a short period of time, and a rubbery or gluey mass is formed and the yield is much lower. It is also preferable to agitate the reactants during the reaction.

The water content of the starting materials or solvent should be kept as low as possible and it is preferable to keep the water content to less than 5%. Larger amounts of water result in the formation of a coloured rubbery or gluey material and in decreased yields of the desired product.

The low-molecular weight product is dried and the hydrogen halide and alcohol removed. If necessary, the product can be finally neutralised with a weak base such as sodium bicarbonate.

The low-molecular weight cellulose derivatives obtained in accordance with the present invention can be advantageously employed in fields in which various cellulose derivatives cannot be used on account of their high molecular weight and high viscosity when in solution. Typical fields of application are as coating materials of pharmaceutical or agricultural chemicals, coating materials for tablets, painting materials and film base.

An example of the present invention is shown below:

EXAMPLE

The treatment is performed with 20 kilograms of methylhydroxypropyl cellulose powder (water content: 1.4%, viscosity in 2% aqueous solution: 50 cps at 20° C) and 2 kilograms of anhydrous methanol containing 10% hydrogen chloride in a glass-lined vessel with a glass-lined agitator at 50° C for 3 hours. The molecular weight of the cellulose is reduced to a value of 6.3 cps at 20° C (measured in a 2% solution). After the treatment, the product is discharged from the vessel and dried overnight in an air stream at 60° C, and 5 grams of sodium bicarbonate powder are added and mixed in a blender. There are obtaine 19.4 kilograms of methylhydroxypropyl cellulose of very low-molecular weight.

WHAT WE CLAIM IS:—

1. A method of making low-molecular weight cellulose derivatives by partial depolymerisation, which comprises treating, at a temperature lower than 80° C, a cellulose derivative in powder form, with a solution of a hydrogen halide in an anhydrous C_1 to C_6 aliphatic monohydric alcohol, the proportion of hydrogen halide being less than 5% by weight of the cellulose derivative being treated, and subsequently removing the hydrogen halide at least partly in vapour form.

2. A method according to claim 1, wherein further hydrogen halide is removed by subsequent neutralisation with a weak base.

3. A method according to any preceding claim, wherein the removal of hydrogen halide in vapour form is effected by heating the partially depolymerised product in a warm air stream.

4. A method according to any preceding claim, wherein the hydrogen halide is hydrogen chloride.

5. A method according to any preceding claim, wherein the treatment is carried out at from 30 to 60° C.

6. A method according to any preceding claim, wherein water content of the treatment mixture is not over 5% by weight.

7. A method according to any preceding claim, wherein the cellulose starting material is an alkyl cellulose, a hydroxy alkyl cellulose, a carboxy alkyl cellulose or a mixture of two or more thereof.

8. A method according to claim 7, wherein the cellulose is methyl cellulose or methylhydroxypropyl cellulose.

9. A method according to claim 1, substantially as hereinbefore described in the Example.

10. Low molecular weight cellulose derivatives when prepared by a method claimed in any preceding claim.

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